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Section I

Introduction

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An Engineer Looks at Chemically Resistant Masonry

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INTRODUCTION

Chemically resistant masonry (CRM) is at once one of the oldest and most widely used groups of engineering materials, components and structures currently available to the Materials/Corrosion Engineer. CRM construction includes many diverse non-metallic inorganic and organic materials which can be utilized as independent, self-supporting structures or as protective linings for steel, concrete, wood and other substrates. These versatile composites are often the most cost-effective construction for various industrial applications and, when properly designed and installed, have given reliable, extended service under adverse conditions that are damaging to other major types of corrosion resistant materials (alloys, plastics, coatings).

In general, CRM is characterized by excellent resistance to a broad range of corrosive chemical environments including acids (dilute and concentrated), extreme temperatures (beyond the limits of most common materials), and very good strength in compression (but not in tension). It is mainly this unique combination of superior chemical resistance and high thermal stability that makes CRM so useful throughout the power, steel and metalworking, chemical, pulp and paper, pharmaceutical, food processing and beverage, waste treatment and other industries. In severe environments, such as strong acids, solvents or alkalies at elevated temperatures, CRM may be the only practical solution to these aggressive conditions. Even very exotic, costly and scarce metals and alloys cannot always withstand such exposures, at least not at an affordable price. Some typical industrial CRM applications are floors, trenches, sumps, reaction vessels,

tanks (storage, plating, pickling), scrubbers, ducts, stacks, chimneys and other air pollution control equipment.

Since a prime objective is to select and use the optimum (cost-effective) material, component or system for each application, CRM should be carefully evaluated and compared with other corrosion resistant materials to best achieve this long-term economic goal. While the total installed cost of any industrial plant construction is important, the acceptance criterion for a successful materials composite such as CRM should be trouble-free performance and protection with minimum maintenance for a prolonged duration. That is, the optimum engineering structure (e.g., CRM) is the one that best meets the design requirements at the least overall cost. For plants such as nuclear and fossil fuel power stations, the design life ranges 30–40 years; and the daily lost or purchased power cost of a forced (unscheduled) outage due to a critical component failure is astronomical. Accordingly, materials reliability far overshadows its initial capital cost, and the cheapest material often proves to be the most expensive to the plant owner. A similar precaution is necessary when considering low bid installation contractors, unless they are previously qualified based upon a long track record of successful case histories involving the same generic materials and products specified for the application.

DEFINITION AND TYPES OF CHEMICALLY RESISTANT MASONRY

To quote the editor[1] CRM may be defined as "a structure composed of nonmetallic, chemically inert masonry units such as brick, stone, block or other aggregate bonded together with a mortar or mortars of adequate adhesion to the units and possessing suitable chemical and thermal resistance for the anticipated exposure. Such a structure may be assembled from units and mortars of a single type or from a combination of several different types of such units and mortars in order to achieve optimum and most economically satisfactory results." CRM structures as such comprise three components: (1) Masonry units such as brick or tile; (2) Mortars to bond them together, and (3) Membranes to attain a liquid-tight, fully resistant system. All of these components are available in various forms and are produced from many different materials. All three components must be chosen to meet both the environmental conditions and the design requirements of each application.

There are two general categories of CRM construction:

(1) *Load bearing structures* with suitable physical, mechanical and chemical resistance properties to withstand corrosive service conditions. One example of a load bearing CRM structure is an independent, free standing chimney liner made of acid resistant brick and mortar. The tallest known acid brick chimney lining in the United States is a 900-foot high fireclay brick liner in a 1,000-foot high reinforced concrete chimney (Figure 1-1). This two unit coal-fired power station operates on high sulfur coal and emits hot corrosive flue gases from a wet lime flue gas desulfurization (FGD) system incorporating both particulate and sulfur dioxide (SO_2) scrubbing. Moreover, acid brick chimney liners greater than 1,000 feet in height are designed and used successfully in Europe and other parts of the world.

(2) *Linings* to protect floors, vessels and other equipment subjected to corrosion, erosion, abrasion and/or thermal attack from chemical environments. The most common substrates for CRM linings are carbon steel and concrete, but other structural materials such as wood and plastics may also be effectively protected. CRM linings can provide any one or all of the following protection modes: (1) Barrier to control physical or mechanical damage such as abrasion or wear; (2) Thermal insulation effects by limiting the substrate and membrane temperature to prevent thermal damage; and (3) Reduce permeation of corrosive fluid to the substrate, thus minimizing its corrosion rate. CRM linings, such as acid brick and monolithic cements, also prevent "wash", which is the removal of the membrane or substrate corrosion products by the circulating medium. Even when the fluid eventually reaches the membrane or substrate surface, the amount is relatively small, thus limiting chemical attack, and any corrosion products are trapped beneath the masonry shield.

By analogy, carbon steel immersed in *stagnant* seawater corrodes at an average rate of only about 5 mils/year (mpy), discounting pitting, because its undisturbed corrosion products are semi-protective. However, when subjected to *flowing* seawater, mild steel corrodes at a much higher rate because the water velocity and attendant turbulence erodes away the hydrated rust layer and attacks the freshly exposed steel surface. Hence, bare steel piping cannot economically handle seawater at normal pipe design velocities. Either a protective pipe lining must be used or a more erosion-corrosion resistant alloy or fiberglass reinforced plastic (FRP) pipe employed for a reasonable service life. Likewise, the CRM sheathing enables the barrier membrane to perform its primary function of protecting the substrate from chemical corrosion while blocking removal of corrosion products.

CRM structures as installed consist of three component parts: (1) External structural support (e.g., steel, concrete, wood, plastic); (2) Fluid-tight membrane; (3) Non-metallic masonry unit and bonding mortar shielding the membrane. The choice of the materials used in each of the components depends upon the following factors and conditions: (1) Chemicals and their concentrations, encompassing all major constituents and any trace impurities and cleaning agents; (2) Ranges of pH and total acidity or alkalinity; (3) Temperature ranges, including transient thermal cycles and excursions; and (4) Physical effects such as impact, wear, abrasion and positive or negative (vacuum) pressure. The rate of change of pressure or temperature (e.g., thermal shock) must also be considered in evaluating materials for CRM structures. Rapid fluctuations in any of these variables can significantly affect the selection, design and performance of the CRM components. In some cases, operational shocks could be the controlling element in determining the useful life of a CRM structure. To avoid a premature failure, the CRM structure must be capable of resisting any or all of the stresses, strains, static or dynamic loads and other service conditions imposed on it.

To illustrate, in a fossil fuel power plant the loss of boiler air preheater(s) can create a sudden increase in flue gas temperature from $\leqslant 300^{\circ}F$ up to 500°-$700^{\circ}F$ for a brief (e.g., 20-30 minute) period. (Air preheaters are energy conserving heat exchangers that heat incoming boiler combustion air with hot boiler flue gas which is thereby cooled prior to particulate scrubbing. If an air preheater fails, the hot flue gas will not be cooled by the heat transfer to the in-

coming boiler combustion air, and will enter the scrubbing system at the higher temperature.) Should this rare accidental event occur, materials and linings in the FGD system ducts and chimney liner must be able to survive this rapid transition (thermal shock) without substantial structural damage–i.e., preserve plant integrity. For this and many other reasons, CRM structures and linings offer inherent advantages over less thermally stable materials such as coatings and FRP. With very few exceptions, notably the fluoropolymers (Teflon®, Kynar®, Viton®), even the best protective coatings and FRP have upper thermal limits of 250°-350°F, while some CRM materials can endure temperatures up to 1000°-2000°F, well above the worst-case single or double air preheater failure scenario.

Before reviewing the basic CRM materials, these four design limitations for CRM construction must be recognized and addressed by the specifier and end user: (1) CRM structures, like concrete, have excellent compressive strength and thus have good load bearing properties; (2) Conversely, CRM structures are weak in tension, shear and torsion, requiring that they be reinforced or supported by suitable substrates (e.g., steel) to withstand such loads; (3) CRM structures are relatively rigid and brittle and tend to break, rather than flex, when bent; and (4) A structure composed of such units cannot restrain a fluid head. For such a container to be liquid tight and function properly, it must be supported by an outer shell to take the thrust and a liquid tight barrier or membrane behind the brick. For example, a circular duct or cylindrical (or spherical) tank would be the optimum design for a CRM lining as it would keep the masonry lining in compression. All of these design characteristics of CRM structures will be detailed later in a separate chapter. Suffice it to say for now, these fundamental guidelines must be faithfully observed to realize the manifold benefits of CRM construction.

CHEMICALLY RESISTANT MASONRY COMPONENTS AND MATERIALS

The major CRM components and materials will be generally described, followed by some industrial applications of CRM structures and protective linings. Each generic type of CRM component and related materials will be discussed in detail elsewhere by leading specialists in the CRM field. Hence, this section will briefly review the three basic building blocks of the composite CRM structures and linings. As stated, CRM construction incorporates three major components: (1) Primary membrane applied to a structural substrate; (2) Chemical resistant brick or tile to protect the membrane chemically, thermally, and mechanically; and (3) Chemical resistant mortar or grout for bedding and jointing the brick or tile.

The general categories of CRM components detailed in this handbook are: (1) Membranes; (2) Masonry units; (3) Mortars and grouts (for tile); (4) Castables, grouts and polymer concretes; (5) Monolithics; and (6) Expansion joint compounds. (A monolithic lining applied over a membrane coated substrate would also constitute CRM.) Only the first three of these CRM component classes will be discussed below–namely, membranes, masonry units and mortars. Each of these components is available in a variety of forms, shapes, sizes and materials including both inorganic and organic compounds, even metallic

(e.g., lead). Most of the organic materials are high molecular weight polymers or resins with excellent resistance to a wide range of chemicals within their specific thermal limits. By contrast, the inorganic alkali silicates used as mortars and monoliths offer outstanding high temperature resistance in virtually all media except acid fluorides (HF) and strong alkalies (NaOH). For these exposures carbon brick joined with carbon filled furan mortar is effective. Chemically almost any environmental condition can be handled by suitably designed and installed CRM components. It is essential that the above four design guidelines or limitations of CRM materials and components be closely followed for a successful application. The principal CRM components and materials will now be reviewed along with their functions in forming the CRM structures and linings.

Membranes

A membrane is a key material that serves as fluid-tight barrier between the somewhat permeable CRM lining and the substrate or supporting structure. The selection of a good membrane depends upon these major facors; (1) Chemical composition and temperature of the environment, (2) Substrate rigidity, (3) Maximum economic brick thickness that can be installed, (4) Internal pressure, and (5) Unprotected corrosion rate of the substrate in the chemical. A CRM membrane applied to a properly cleaned (often primed) steel or concrete substrate is the "last line of defense" in protecting that substrate from accelerated chemical attack and premature failure. Hence, effective membranes must have both high chemical resistance to corrosive fluids and low permeability to the same media, along with good adhesion to the substrate. Therefore, an elastomeric membrane used under an acid brick lining to control acid corrosion of a carbon steel tank must not only resist attack by the corrosive but be a complete barrier to any of the corrodent that has migrated through the brick and mortar. It is necessary but insufficient that the membrane remain intact and unaffected; it must also prevent the corrosive from reaching the substrate or at least limit its diffusion to a tolerable rate. While the masonry units (brick or tile) protect the membrane against excessive temperature and physical abuse, the membrane in turn guards the substrate against environmental damage. This is a classic example of synergism in which the properties of complementary materials are effectively combined into a very useful composite.

Membranes, which include both liquid applied and solid sheet linings, can be classified as: (1) True membranes that are completely impermeable barriers to specific corrosives, or (2) Semi-membranes which allow a low but acceptable amount of the chemical to reach the substrate. Further, these membrane types may be divided into rigid and non-rigid materials. The rigid membranes include epoxy, phenolic, polyester and furan resin coatings, glass linings, unplasticized polyvinyl chloride (PVC) sheet, and both flake glass filled and fiberglass cloth or mat reinforced epoxy, polyester and vinyl ester resin linings. Non-rigid membranes include hot applied asphalt, the most widely used membrane on concrete substrates (but not on steel); asphalt mastic and bitumastic epoxies; plasticized PVC; and a wide variety of sheet (and some liquid) elastomers including natural rubber, neoprene, butyl, chlorobutyl, Hypalon®, ethylene-propylene, Viton® and polyurethane. Natural and synthetic rubbers are the most common membrane materials for steel substrates. Fluorocarbon (e.g., Teflon®, Kynar®) sheet

linings and baked coatings are employed as membranes for very corrosive processes. These fluoropolymers are almost chemically inert and are the most heat resistant of the organic membranes but have high thermal expansion coefficients and require chemical etching for good adhesion to overcome their anti-stick properties. When flexible membranes with superior chemical and heat (to 400°F) resistance are needed, fluoroelastomers such as Viton® and Fluorel® should be considered. Liquid applied coatings based upon Viton® are now available in addition to sheet membranes. Metallic sheet membranes are also utilized including lead, chromium-nickel (austenitic) stainless steels and other corrosion resistant alloys. All of these and other membrane materials (e.g., porcelain enamel, glass lining) and their selection for CRM applications are detailed in subsequent chapters.

Masonry Units

Masonry or construction units, like membranes, are vital components in CRM construction. ASTM defines a chemical resistant construction unit as "a modular non-metallic material, either vitreous or nonvitreous, used in industrial processes primarily for applications where chemical, thermal and mechanical resistance is required." Masonry units are used both in CRM structures such as free standing acid brick stack liners and in CRM linings such as acid brick or tile linings for floors and process vessels. If fluid (liquid or gas) barriers are required, masonry units should be used in conjunction with membranes applied directly to properly prepared substrates. Most masonry units are installed by laying the brick or tile with a suitable chemically resistant mortar or grout chosen to resist the environmental conditions. There is a great variety of masonry units available for various industrial applications requiring superior resistance to chemical corrosion, erosion, abrasion, wear and/or elevated temperatures. Practically, no other generic class of engineering materials can withstand such a broad array of adverse conditions as well as the right combination of CRM units, mortars and membranes. These CRM composites are effective against corrosive acids, alkalies, salts and solvents over the wide range of pH, concentrations and temperatures found in industry.

Masonry units used in CRM construction encompass the following basic types: (1) Acid brick (red shale, fireclay); (2) Carbon brick; (3) Foamed borosilicate glass block; (4) High alumina and insulating brick; (5) Silica brick; (6) Special composition brick and block (porcelain, basalt, silicon carbide, granite, press-molded hydraulic); and (7) Tile (quarry, ceramic, glazed porcelain). Each of these masonry units has its particular area of utility in CRM construction. Among these diverse CRM units, industry can combat virtually all chemical and thermal exposures within the design limitations of CRM linings and structures. In chemical services that are also abrasive, these CRM bricks would rank in abrasion resistance as follows: high alumina (best), silicon carbide, hard burned fireclay, and red shale.

Acid Brick: Acid brick, also called acid resistant or acid proof brick (covered by ASTM C279), are of two major types: (1) Red shale, the predominant brick in CRM construction; and (2) Fireclay, another common brick in CRM applications. These two acid brick are the most widely used masonry units in CRM structures and linings, including floors, trenches, sumps, vessels and chimney

liners. Both types of acid brick are made from selected clays or shale containing little acid-soluble constituents and are fired in kilns at higher temperatures and for longer times than ordinary face brick. This produces a much stronger, denser brick with far lower water absorption and superb resistance to most acids except hydrofluoric (HF), which requires carbon brick. Red shale brick is higher in silica and iron content, while fireclay brick contains more alumina. The generally denser shale brick normally shows lower water absorption and better sulfuric acid resistance than fireclay brick, which has somewhat greater thermal shock resistance (less brittle) than red shale brick. Because of the low (<1%) absorption of Type L (usually red shale brick), these bricks are more often used in process vessels and other applications demanding maximum acid resistance and minimum absorption. However, fireclay brick can also be manufactured to meet the 1% absorption and 8% acid solubility limits of Type L shale brick. The lower iron content of the buff-colored fireclay brick is beneficial in certain industrial processes. For example, one sulfuric acid plant producing 98% sulfuric acid guarantees a maximum iron content of 25 ppm, in which fireclay brick and potassium silicate mortar are employed as a fully resistant, non-contaminating CRM construction.

In sulfuric acid production, acid brick lining of membrane coated mild steel tanks and reaction vessels is considered the most durable and versatile construction material for the sulfuric acid plant. Such linings will reduce the steel shell temperature and prevent erosion of the normally protective iron sulfate film that forms in stagnant, concentrated (oxidizing) sulfuric acid. Dilute (reducing) sulfuric acid solutions are very corrosive to carbon steel, which must be protected by impermeable (e.g., elastomeric) membranes and acid brick lining systems. Such acid brick linings often employ membranes comprising a thin film of Teflon® or Kynar® sandwiched between layers of asphalt mastic.

In phosphoric acid production plants, both red shale and fireclay brick have excellent resistance to all concentrations of phosphoric acid at temperatures up to 250°F, provided the acid contains no HF. If HF is present in the phosphoric acid, carbon brick construction must be used. As a rough rule-of-thumb, HF levels above 50 ppm in phosphoric acid require tank linings of carbon brick bonded and jointed with a carbon (or barytes) filled furan mortar over a suitable membrane to match the steel or concrete substrate structure.

ASTM specifications on acid brick include: (1) C279, Chemical-Resistant Masonry Units, which covers Types H and L brick; (2) C410, Industrial Floor Brick, covering Types H, L, M and T brick; and (3) C980, Industrial Chimney Lining Brick, which concerns solid kiln-fired brick made from clay and/or shale suitable for use in masonry construction in contact with the chemicals present in the flue gases found in industrial chimneys. All of these brick types will be fully described in later chapters. The newer ASTM C980 specification covers three acid bricks: (1) Type I (old H), for use where low absorption and high acid resistance are not major factors; (2) Type II, for use where lower absorption and higher acid resistance are required; and (3) Type III (old L), for use where lowest absorption and highest acid resistance are required. ASTM C279 has been revised to adopt these three acid brick types.

Carbon Brick: Carbon brick, though costing much more than acid brick, is required in some CRM applications because of its high resistance to HF and con-

centrated alkalies such as caustic soda (NaOH). Red shale and fireclay bricks are not compatible with strong alkalies and are attacked by acidic fluorides above certain threshold concentrations. Currently economically allowable acid fluoride (HF) levels are judged to be under 50 ppm in immersion service and 1,500 ppm in wet-dry conditions. However, recent long-term HF test programs of various CRM materials indicate they might tolerate slightly higher acid fluoride limits without significant damage. This greater tolerance of HF has been observed in power plant chimney liners made of acid brick and potassium silicate mortar handling flue gases from coals containing fluorides. Despite acidic fluoride concentrations well above the 50/1,500 ppm range in some FGD systems, the acid brick chimney liners are performing well with little or no HF attack. Nevertheless, carbon brick offers excellent resistance to the two media, HF and NaOH, detrimental to acid brick, silicate mortars and monolithics, and silica filled resins.

Carbon brick differs from acid brick in other respects: much higher absorption, generally lower thermal expansion coefficient, superior shock resistance (less dense), and much higher thermal conductivity (K factor). Because carbon brick is more conductive than acid brick, thicker carbon brick tank linings frequently must be used for equivalent thermal insulation over the membrane/substrate. This greater lining thickness further increases the higher price of carbon versus acid brick linings, but in some environments only carbon brick will work. Carbon brick is often used with carbon filled furan resin mortar for floors or vessels exposed to hot aggressive chemicals such as HF and NaOH. Another difference in the two CRM bricks is the much lower thermal limit ($\approx$750°F in the presence of oxygen) of carbon brick due to its susceptibility to strong oxidizing conditions in combination with heat (e.g., nitric acid, concentrated sulfuric acid). By contrast, acid brick can readily handle service temperatures well above 1000°F, even to 2000°F, whether in oxidizing or reducing acid environments.

Foamed Borosilicate Glass Block: This thermally insulating closed cell foamed glass block lining, commercially introduced in recent years, has found increasing usage in many industries because of several unique properties: outstanding chemical resistance (except to HF and NaOH), thermal resistance up to 960°F, very low K factor (excellent insulator), impermeability, good thermal shock resistance and very light weight. The foamed glass block comes in many standard sizes (common lining thickness is 1½") and is bonded to itself and the substrate by an asphalt-urethane adhesive/membrane or an acid resistant mortar. Since this glass block lining is such an efficient thermal insulator, it provides very effective internal insulation to a steel tank or duct. Its light weight, only 12 pcf (8-12% the density of cementitious linings), is another design benefit in reducing dead loads on lined structures. The installed weight of only 2-3 psf is similar to flyash design loadings and permits retrofits to existing plant ductwork and stack liners with little or no structural modifications. Two major advantages of the borosilicate glass block versus gunned monolithic silicate linings are its lower permeability and virtual immunity to cracking. This block lining has performed well for several years in the outlet ducts and chimneys of a number of air pollution control facilities including electric utility FGD systems, pulp and paper mills and municipal and industrial incinerators.

High Alumina and Insulating Brick, Silica Brick, and Specialty Brick and Block: These special composition brick and block are employed for specific applications as outlined below:

High Alumina Brick: This 90-99% Al_2O_3 brick is used as refractory brick to resist extreme temperatures ranging 2000°-3000°F. Insulating firebrick is generally light weight and somewhat porous with the higher alumina than silica content used for the highest temperature ranges to 3000°F, and the higher silica than alumina compositions used below 2000°F.

Silica Brick: Brick containing about 99% silica is favored over acid brick for very high acid concentrations, especially phosphoric acid.

Specialty Masonry Units: These include: (1) Porcelain, an 85% alumina, very hard and dense brick, good to 1500°F, very cleanable with nil absorption; (2) Basalt, an extremely dense and costly cast block, having outstanding abrasion resistance, used for bottom ash slurry linings, coal/ash hoppers, bunkers and chutes; (3) Silicon carbide brick, noted for its excellent resistance to abrasion and elevated temperatures; (4) Granite block, one of the oldest but now seldom used natural stone units–its high density makes bonding at joints difficult; and (5) Press-molded hydraulic bonded brick, a special brick designed for caustic and alkaline bleach solutions and bonded with a hydraulic mortar meeting ASTM C398 requirements.

Tile: The three types of chemical resistant tile are quarry, ceramic and glazed porcelain. Tile is chemically similar to, but thinner than, acid brick and is distinguished from it as follows: (1) Tiles are masonry units $\leqslant 1\frac{1}{4}$" thickness, while (2) Bricks are masonry units $> 1\frac{1}{4}$" thickness. (This is roughly analogous to the distinction between metallic sheet (or strip) at $\leqslant \frac{3}{16}$" and plate $> \frac{3}{16}$" thickness.) Packing house or dairy tile (pavers), usually made from red shale clay with a higher (5-6%) absorption than red shale brick, is set on a bed of CRM grout over a membrane and the open joints filled by grouting. Quarry and ceramic tiles fired from the same clays and shale as acid brick are widely used to protect all types of concrete floors and walls in various industries from corrosive chemicals, with the same media restrictions (to HF & NaOH) as acid brick. Quarry, glazed tile and ceramic tile (all units under 1" thick) must be bonded directly to the substrate with an adhesive that also serves as the membrane. Units thinner than 1", when laid over a soft membrane such as asphalt, tend to break up under traffic, even foot traffic.

Mortars and Grouts for Brick and Tile

Chemical resistant mortars for acid or carbon brick and grouts for tile are the third important component and complete the three part CRM composite. The most durable CRM structures and linings utilize impervious membranes against a substrate sheathed with masonry units bonded with mortars or grouts. Depending upon the service conditions, the brick or tile may be applied directly onto the primary membrane or over a bedding layer of mortar or grout troweled onto the membrane surface. The CRM mortars and grouts used with masonry units fall into three generic classes: siliceous, resinous, and sulfur. Resinous mortars used in CRM construction include phenolic, furan, epoxy, polyester and vinyl ester resins. The proper selection of these chemical resistant bonding agents with the appropriate brick or tile will resist any hot corrosive environment encountered in industry. When the optimum CRM materials are installed by a skilled, experienced contractor, the net result is the most cost-effective anticorrosion system currently available.

Silicate Mortars: The major inorganic silicate ("water glass") mortars are based upon sodium or potassium silicates cured with various organic or inorganic acidic catalysts (hardeners, setting agents). Perhaps the best of these products are those containing no fluorides, employing other types of hardeners. All of these alkali silicate mortars are very heat resistant, some up to about 1750°F and are fully acid resistant below pH 7 except to HF and acid fluoride salts above certain threshold concentrations. Some silicate mortars are considered resistant to mild, dilute organic bases to pH 8, possibly pH 9, depending upon the specific base. Sodium silicates are susceptible to sulfation-hydration reactions when contacting hot sulfuric acid and thus are the least suitable mortars for acid brick stack liners handling wet sulfur oxide-laden flue gases and acid condensates from utility boilers. Since potassium silicate mortars are not subject to this growth type reaction, they are more commonly used in hot, strong sulfurous and sulfuric acids and are the standard mortars for acid brick in power plant chimney liners. However, potassium silicates are subject to the formation of other growth salts, particularly alums, in the presence of sulfuric acid *and* iron, aluminum or magnesium. In such combinations, a silica, rather than silicate mortar may be considered. The best potassium silicate mortars are free of sodium, calcium and fluorides. Both single and two component systems are available to industry. Silicate mortars are the most absorbent and thus the most permeable of all acid resistant mortars. Only hydraulic mortars have higher absorptions than silicates.

Silica Mortars: Silica mortar is a strictly acid and heat resistant material, handling all acids except HF and acidic fluorides at pH 0-7 and thermally stable up to 2000°F. A relatively recent self-curing silica mortar contains only borosilicate glass powder, silica sol and crushed silica with no metallic constituents. This avoids both the sulfation-hydration reaction of the sodium silicates and the alum formation problems of the potassium silicates. Like the silicate mortars, silica mortars also resist organic chemicals.

Sulfur Mortars: Hot melt-and-pour sulfur mortars are ancient, doubtless one of the oldest of all chemical resistant materials still used today. They are very resistant to non-oxidizing acids and weak alkalies below 200°F over a pH range of 0-12. Three types of sulfur mortars are typically employed: (1) One containing an all-silica filler with minimum plasticizer, used to bond acid brick; (2) A mortar with an all-carbon filler and minimum plasticizer, used primarily to lay carbon brick for nitric-hydrofluoric acid pickling tanks (to clean stainless steels) and the underlying floors; and (3) A much more flexible all-silica filled product with double the amount of plasticizer of the other two mortars, used to join vitrified clay (terra cotta) pipe conveying waste acids and other effluent chemicals, and to assemble "pole line hardware" for the power industry.

Resin Mortars: The following organic/polymeric mortars are used in CRM construction, all being usable in HF exposures if non-silica fillers such as carbon or barytes are employed:

Phenolic Mortars: Phenolics are the oldest resinous mortars used with acid brickwork. The original phenol-formaldehyde materials have an effective pH range of about 0-10. They are very resistant to dilute and concentrated non-oxidizing acids, solvents and dilute alkalies. Modified phenolics further increase this pH range. Such mortars raise the maximum pH well above the normal pH 0-12 range, and are the only resin-based mortars resistant to aniline. Phenolics are useful up to an upper service temperature of 360°F.

Furan Mortars: Furans have the broadest range of resistance to both acid and alkali (pH 0-14) and temperatures of all the resin mortars. Furan mortars can accept temperatures up to 350°-360°F. Modified furans are available that can withstand continuous temperatures of up to 425°F and intermittent temperatures to 475°F. Unlike the other mortar materials, furans have excellent resistance to strong alkalies as well as non-oxidizing acids and many organic chemicals. However, furan mortars are attacked by some organic solvents such as aniline. Furans are available with silica, carbon or barytes fillers, the filler choice depending upon the environmental conditions.

Epoxy Mortars: Epoxies are the strongest resin mortars, have the best bond strength to other CRM materials, and resist many solvents, mild to moderate acids, non-oxidizing and alkaline media. Their useful pH range is about 2-14, and their thermal limit is approximately 230°F. Besides their excellent alkali and dilute acid resistance, epoxy mortars handle many organic chemicals and sodium hypochlorite at low temperatures. Epoxies should not be exposed to acetic acid and its esters. Epoxy mortars have the best physical and mechanical properties of all the resin mortars.

Polyester and Vinyl Ester Mortars: These two mortars, of which there are many types, are suitable for a pH range of about 0-11 and a continuous service temperature of 225°-230°F. The two related resins, which complement the epoxy resins, resist dilute and concentrated acids and weak alkalies. Their resistance to acid bleaches such as chlorine dioxide and to oxidizing acids such as nitric and chromic is superior to that of other resinous mortars, and they are excellent in acetic acid and related esters. However, polyester and vinyl ester mortars are the poorest resin mortars in other organic chemical exposures including solvents in general. Such mortars are widely used in paper mills and are suitable with acid brick or ceramic tile in the lower temperature zones of mildly acidic utility FGD systems.

Hydraulic Mortars: The two common types of hydraulic (water cured) cements or mortars are portland cement, the basic lime-derived cement used in structural concrete (five types per ASTM C150), and calcium aluminate (e.g., Lumnite). Portland cement normally contains $<5\%$ alumina, while Lumnite has $>30\%$ alumina. Chemically, portland cement mortar or concrete is not resistant to acids, being limited to pH $\geqslant 6.0$, whereas Lumnite resists dilute acids to about pH 4.5, below which it is attacked too rapidly for practical use. Various latex modified or augmented portland cement concretes have been developed to improve its neutral and alkaline corrosion resistance, either by densifying the concrete or by coating the reactive components. For example, latex impregnated concretes have been used on northern bridge decks to better resist deicing salt/chloride corrosion of the steel rebars and attendant spalling of the reinforced concrete decks. (Elastomeric membranes, epoxy coated and galvanized rebar, calcium nitrite corrosion inhibitive admixture and cathodic protection have also been effective in concrete bridge deck protection.)

Another version of portland cement mortar or concrete is the replacement of some of the portland cement with rice hull ash. This ash additive markedly improves the resistance of the mortar or concrete to food acids and similar chemicals. Flyash (pozzolanic admixture) meeting ASTM C618 has also been widely used to improve the properties and sulfate resistance of portland cement

concrete. It should be noted that ASTM C150 Types II and V portland cements, while much more sulfate resistant, are no more acid resistant than ordinary Type I portland cement. Although Type II and V based concretes and mortars are substantially better in neutral or alkaline sulfate solutions, they would be destroyed by sulfuric acid and its acid salts. Mortars based upon Lumnite, aluminum silicate and calcium silicate extend economic sulfuric acid resistance down to approximately pH 4[5] (fairly dilute mineral acids). For stronger acids below about pH 4,[5] the mortar selection would involve one of the acid resistant inorganic or organic materials described above, depending upon the acid type, concentration and temperature.

All of these materials–brick, mortars and membranes–will be fully discussed in later chapters along with (1) Castables, grouts, and polymer concretes; (2) Monolithics (troweled, sprayed and gunned linings); and (3) Expansion joint compounds, plus rigid plastic fabrications such as polyethylene, polypropylene and PVC. These components made from a whole host of materials are effectively used in a wide variety of industrial applications requiring superior chemical and thermal resistance.

In closing this section, the energy conservation aspects of CRM construction should be cited as a principal benefit. Because all CRM linings are internally insulating to varying degrees, CRM lined equipment will operate cooler and more efficiently while the costs and maintenance of external insulation are saved. With the thermal insulation (CRM lining) inside the duct or vessel, it is subject to less damage than external insulation. When closed cell borosilicate glass block lining is employed, no external thermal insulation is needed for the lined steel structure, simply a suitable thin film exterior coating such as an epoxy, vinyl or aliphatic urethane. In addition, plant personnel are safeguarded by the moderate outer steel surface temperature resulting from the insulative CRM lining. The energy and materials savings realized from this internal CRM design merit serious consideration.

CHEMICALLY RESISTANT MASONRY APPLICATIONS

The industrial applications of CRM linings and structures are both numerous and varied. This handbook could be filled with countless CRM case histories from around the world. There are a number of excellent publications available to the interested reader (see Bibliography at end of this chapter). In general, any industry requiring reliable, long-term chemical and thermal resistance does or should use one or more types of CRM construction. Cheaper, less durable engineering materials and components have been used but are seldom as cost-effective as CRM systems. In some severe environments at elevated temperatures, CRM construction is the only viable or practical solution. Since the author's chief experience with CRM structures and linings has been in the fossil fuel power generation industry, especially in air pollution control systems, the following discussion will emphasize these CRM application areas. Certainly, the many CRM uses in other industries are no less important and are detailed elsewhere in this handbook as well as in the open literature.

Power Industry–Flue Gas Desulfurization Systems

Electric utility FGD systems pose many difficult operating and maintenance problems to the owner and his architect/engineer and constructor, not the least of which are corrosion, erosion and abrasion effects from high velocity flyash-laden flue gas, scrubber and flyash slurries, chlorides, fluorides, sulfurous (SO_2), and sulfuric (SO_3) acids over a wide range of temperatures. Though the process slurry in the SO_2 scrubber (absorber, spray tower) is controlled at a normal pH 5.5-6.5 at moderate temperatures of 120°-135°F, the wet scrubbed gases leaving the mist eliminators still contain up to 10% of the inlet flue gas SO_2 content plus some SO_3, halides (Cl, F) and flyash at an uncontrolled pH. When this gas mixture enters the outlet ducting and is reheated with hot (300° ± 25°F) bypass flue gas to temperatures ranging 150°-200°F or higher in the duct mixing zone region, a very corrosive mixed gas/condensate condition below the acid dew point develops in the outlet ducts and full chimney height. It has been well established that the post-scrubber portion of the FGD system–i.e., outlet ducts and chimney liner–are the most severe environmental zones and the highest maintenance areas. A wide variety of materials (alloys, FRP, organic linings) have been used with mixed success downstream of the mist eliminators and outlet dampers, CRM construction has generally performed the best in this extremely hostile region of the FGD system. This is especially true of power plant chimney liners, where acid brick linings with pressurized annuli have proved more reliable than coated steel or FRP liners in FGD systems employing hot bypass reheat operation.

In addition, non-metallic inorganic materials have been used in FGD system prescrubbers, spray nozzles and slurry pumps. The favored CRM materials include acid brick, chemical resistant mortars and chemically bonded (cast or gunned) cements, used as monolithic linings for their high chemical, thermal and/or abrasion resistance. Hard, dense pre-fired shapes of alumina and silicon carbide are employed for abrasive/erosive slurry spray nozzles and slurry pump components. Acid brick bonded with potassium silicate mortar is the preferred construction for chimney liners or flues. Venturi throats of SO_2 scrubbers have been lined with high alumina or silicon carbide bricks, which resist hot sulfuric acid and are more abrasion resistant than acid brick. Hydraulic cement linings are sometimes used to protect steel prescrubbers (quench zones) in FGD systems. These typically contain calcium aluminate or aluminum silicate cements that are rapidly attacked by sulfuric and other acids below pH 4.5. Because of the controlled, mildly acidic pH in the SO_2 scrubbers, gunited hydraulic cements are often used in the prescrubber area. However, chemically bonded cement linings based upon sodium or potassium silicate are much more acid and heat resistant and thus would better handle system upsets in pH and temperature. Some completely non-metallic SO_2 scrubbers are now built of concrete lined with chemical resistant ceramic tile. For any of these gunned cementious linings or the tile lined concrete to work properly, the gunned or tile lining must be applied over impervious membranes well bonded to a suitably prepared, preferably blast cleaned, steel (or concrete) substrate. Even the best potassium silicate-based lining is permeable and may crack from thermal and vibrational stresses, thus exposing the steel substrate to rapid attack by acid condensates unless pro-

tected with an impermeable, acid-resistant membrane. Such cracking can be minimized by using properly spaced corrosion resistant alloy stud anchors, which distribute the stresses.

Specific Power Plant FGD System Experience

The extensive in-plant testing, evaluation and use of CRM linings and structures at a high sulfur coal-fired power station amply demonstrate the utility and effectiveness of many types of CRM components, which are successfully used in most utility FGD systems and other air pollution control facilities.[2,4,14,22] This large steam electric generating station features twin units located in a river valley, requiring two 1,000 foot high chimneys to adequately disperse the scrubbed flue gasses (Figure 1-1). The power boiler flue gases are cleaned by a highly efficient FGD system comprising: (1) Electrostatic precipitators to remove essentially all of the particulates (flyash), followed by (2) Lime slurry-based SO_2 scrubbers to remove over 90% of the SO_2 from the flue gas. The wet scrubbed flue gases containing various levels of SO_2, SO_3, Cl, F and flyash then pass through

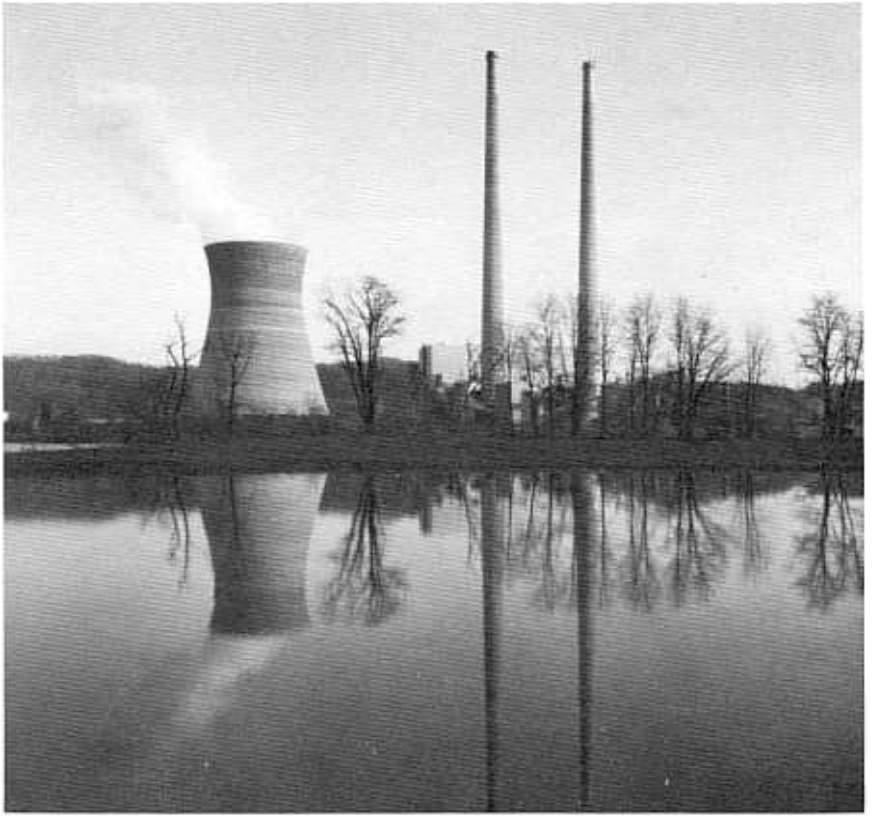
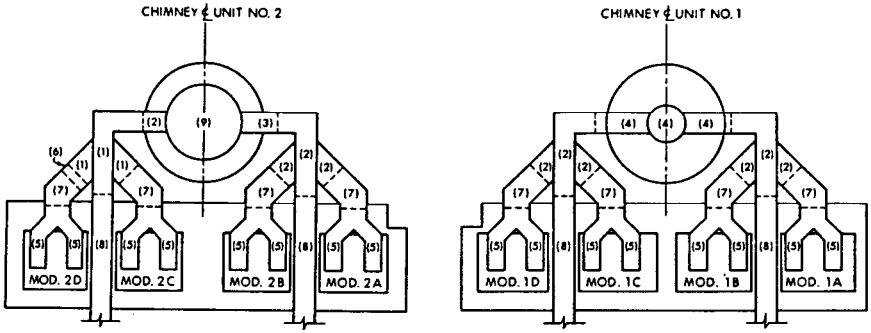


Figure 1-1: Large coal-fired power station with FGD system and two 1,000 foot high chimneys, one containing the tallest acid brick liner in the United States.

FRP mist eliminators, enter lined steel ducts which join a scrubber bypass reheat duct, through turning vanes (mixing zone region), into the chimney breeching (100 foot elevation), and up the 900 foot high chimney liner to the atmosphere. All lined rectangular ductwork and the internal bracing were fabricated of welded ASTM A36 carbon steel plate or pipe, while each 1,000 foot high chimney was constructed of reinforced concrete with an independent protective liner. [The preferred design for CRM linings is cylindrical ducting with external (no internal) stiffeners.]



(1) VINYLESTER COATED-CHEMICALLY CURED COLLOIDAL SILICA CEMENT OVER VINYLESTER.

(2) POTASSIUM SILICATE CEMENT OVER VINYLESTER.

(3) SODIUM SILICATE CEMENT OVER VINYLESTER.

(4) VINYLESTER COATING.

NOTES: MODULES 1A/D AND 2A/D ARE SO_2 ABSORBERS. ALL LININGS APPLIED OVER A-36 CARBON STEEL PLATE.

(5) NATURAL AND CHLOROBUTYL RUBBER.

(6) BOROSILICATE GLASS BLOCK ON ASPHALT-URETHANE ADHESIVE MEMBRANE.

(7) POTASSIUM SILICATE CEMENT ON VINYLESTER ON FLOOR. VINYLESTER COATING ON WALL AND ROOF.

(8) UNCOATED BYPASS DUCT.

(9) ACID BRICK (FIRECLAY) LINER.

Figure 1-2: Stack and duct linings. All eight modules are SO_2 scrubber modules.

Figure 1-2 shows the plan view of Units 1 and 2 ducts and chimneys with the various generic CRM lining materials used in different sections of the FGD system. The SO_2 scrubber modules (four/unit) were initially lined with soft natural rubber sheet, which was later upgraded to a slightly thicker, more impermeable and heat resistant chlorobutyl rubber lining. (Chlorobutyl, neoprene and triply (soft/hard/soft) sheet rubber linings are the most commonly used elastomeric linings in wet SO_2 absorbers.) The 1,000 foot Unit 2 chimney was protected with a self-supporting 900 foot acid brick lining. This tallest American acid brick liner was built of modified Type H (or Type II) fireclay brick bonded with a chemically cured potassium silicate mortar containing a silica sand aggregate. This is the preferred CRM materials combination used in such free standing structures. The annulus between the acid brick lining and the outer concrete shell was pressurized by fans to maintain a positive pressure in the annular space greater than the outlet flue gas pressure. Pressurization is standard industrial practice to prevent acid vapors from penetrating through cracks and permeability in the brick/mortar liner and condensing on the non-acid resistant concrete column. In some chimneys, the concrete shell interior is lined with an acid resistant mastic or other protective coating to further retard acid attack of the sus-

ceptible concrete. (Note that the independent acid brick stack liner is one of the few types of CRM construction where a barrier membrane is not necessary, since there is no substrate or supporting structure in this instance.)

This acid brick chimney liner has completely resisted both wet saturated flue gas laden with sulfur oxides, halides and some flyash and hot gases also below the acid dew point over a temperature range of 125°-325°F for over five years. At the higher flue gas temperatures, the condensing sulfuric acid concentrations are estimated to range up to 60-80% in parts of the outlet ducting and chimney lining. Should there be a rare air preheater failure, the flue gas temperature could rise rapidly to either 400°F or 700°F for a brief period. Nevertheless, this well designed and erected acid brick liner with good thermal/shock resistance can safely withstand any transient thermal condition. The Unit 1 chimney liner is carbon steel protected with a sprayed inert pigmented vinyl ester coating. This coated steel liner has also performed well for over six years but requires that the FGD system be operated to avoid thermal excursions—i.e., minimal hot bypass gas flow. Conversely, because of its excellent resistance to elevated temperatures, the Unit 2 acid brick liner has no operational restrictions except for possibly limiting the heating or cooling rates during startups or shutdowns. About the only design limitation of acid brick stack liners is their unsuitability in a high seismic zone.

The scrubber outlet ducts were lined with a variety of monolithic cementitious systems to evaluate their behavior under actual operating conditions. This large scale in-plant test program was designed to determine the most durable gunned lining to combat the same wet and hot corrosive flue gas conditions as in the chimney liners. It was conclusively shown that the much more acid resistant sodium and potassium silicate cements clearly outperformed the hydraulic cement linings such as aluminum and calcium silicates, which were corroded and eroded by the acid condensates and high velocity flue gases. The gunited single component sodium silicate cement lining retained its surface hardness with little attack but sustained cracking, allowing acid corrosion of the steel substrate. The denser sodium silicate cement lining worked well, much better than the modified sodium silicate cement containing light weight aggregates. The 100% potassium silicate-based cement lining performed the best of the gunned monolithic linings, all applied over a sprayed inert filled vinyl ester membrane coating. The spray applied high-build vinyl ester coating without a CRM shield worked well in the lower temperature scrubber outlet ducts (except for physical floor damage), but failed when exposed to the hotter mixed gas conditions. Nevertheless, this inert pigmented vinyl ester system performed very well as an acid resistant membrane under the better monolithic linings where the gunited cement was reinforced with stainless (not carbon) steel stud anchors. For such outlet ducts where the acid condensate measures pH 1-3, corrosion resistant (e.g., T316 SS) welded stud anchors should be used to retain the lining. The borosilicate glass block lining effectively protected the steel ducting from corrosion and abrasion. This lightweight block lining proved so successful that it has largely replaced the gunned potassium silicate cement lining which had been applied to most of the outlet ducts. Although the 100% potassium silicate lining had performed quite well with only minor cracks and repairs, the closed cell foamed glass block lining was considered to be virtually maintenance-free.

The most acid resistant CRM linings and acid brick structures are providing cost-effective protection to the major problem areas of this and many other coal fueled power plant FGD systems.

CONCLUSION

In concluding this overview of CRM, it is recommended that the technical sources listed in the Bibliography be reviewed. In addition, the reader is referred to the following organizations:

(1) The American Society for Testing and Materials (ASTM), Philadelphia, Pennsylvania, with particular emphasis on these ASTM committees:

(a) ASTM C-3, Chemical Resistant Non-Metallic Materials

(b) ASTM C-15, Manufactured Masonry Units

These two ASTM committees have prepared and issued the standard specifications and test methods on CRM materials and components that are used throughout industry.

(2) The National Association of Corrosion Engineers (NACE), Houston, Texas with emphasis on NACE Technical Committees such as Unit Committee T-6K on Corrosion Resistant Construction With Masonry and Allied Materials. The first two reports issued by NACE T-6K were: (1) *Acidproof Vessel Construction With Membrane and Brick Linings*, and (2) *Acidproof Floor Construction With Membrane and Brick*.

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